

N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM
MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT
CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED
IN THE INTEREST OF MAKING AVAILABLE AS MUCH
INFORMATION AS POSSIBLE

University of Pennsylvania
Philadelphia, Pennsylvania 19104

Final Report On

HIGH ELECTRICAL RESISTIVITY
CARBON/GRAPHITE FIBERS

to

NASA Langley Research Center
Hampton, Virginia 23665

(NASA-CR-162909) HIGH ELECTRICAL
RESISTIVITY CARBON/GRAPHITE FIBERS Final
Report (Pennsylvania Univ.) 26 p
HC A03/HF A01

N80-20312

CSCL 11D

Unclas

G3/24 46781

By: F. Lincoln Vogel
Department of Electrical
Engineering and Science

William C. Forsman
Department of Chemical
and Biochemical Engineering

Co-Investigators



ABSTRACT

Carbon/graphite fibers were chemically oxidized in the liquid phase to fibers of graphite oxide. Resistivity increases as high as 10^4 times was obtained, the oxidized fiber decomposed on exposure to atmosphere. A factor of 10^3 remained as a stable increment. The largest change observed was 10^6 times. Best results were obtained on the most highly graphitized fibers. Electrochemical oxidation yielded a lower increase -- about 10 times, but provided a controllable method of synthesis and insight to the mechanism of reaction. Tensile tests indicated that the strength of the fiber on oxidation was decreased by no more than 25%.

INTRODUCTION

Recently, it was found that a dispersion of carbon/graphite fibers in air, as might occur during the burning of fiber-epoxy composites, would cause shorting and arcing problems in nearby electrical equipment. This problem is primarily due to the high electrical conductivity of graphite fibers¹⁻³. It was thus proposed that we attempt to convert the graphite fiber into non-conducting graphite oxide without degrading the mechanical properties of the fiber.

Graphite oxide is one of the two known covalent compounds of graphite. The compound demonstrates high stability at normal temperatures because of its covalent characteristics. Its electrical resistivity varies from 10^3 to 10^7 ohm cm, depending on the carbon to oxygen ratio⁴. No definite stoichiometry can be assigned to the compound but an idealized formula has been postulated as $C_8O_2(OH)_2$ ^{5,6}. The covalent carbon-oxygen-carbon bonds (ether linkage) suggest a puckering of layers. The oxygen atoms, however, can also demonstrate keto-enol tautomerism⁷⁻⁹ which would preserve the planar hexagonal network. Thus, it is expected a priori that a partial conversion of carbon/graphite fiber to the corresponding oxide would provide a balanced solution to the air-born fiber problem, since conversion might not seriously degrade the fiber's mechanical properties.

In the first phase of the study, we successfully obtained a stable oxidized fiber with a factor of 10^3 increase in resistivity by chemical oxidation. However, the chemical method produced erratic results and indicated a poor adaptability to commercial processing. In order to gain a control over the oxidation process the feasibility of electrochemical oxidation was considered in

the second phase of the research. The mechanical properties of the fibers due to oxidation have also been examined.

I. Chemical Oxidation

Materials: The following carbon/graphite fibers were selected for examination: Type P (Union Carbide), GY-70 and GT-30 (Celanese) and HMS and H7 (Hercules). All of these fibers are commercially available and are therefore assumed to be supplied with a surface treatment. The Type P fiber has a pitch precursor whereas for all of the others the precursor is polyacrylonitrile. The variety of fibers employed in the study was intended to give a cross section of those commercially available so that any treatments developed to increase resistivity will have general applicability.

Experimental Procedures: The graphite fiber was oxidized with variations on the method described by Hummers¹⁰. Before experimenting with single, continuous fibers, a few grams of chopped fiber were treated and the onset of oxidation verified by the appearance of a green hue of the suspended product in water. With slightly modified procedures, a single fiber mounted on an alumina substrate with platinum contacts was treated similarly.

Using the Hummers method, the substrate was placed in a 100 ml beaker with 10 ml concentrated sulfuric acid and 0.25 g of sodium nitrate. Slowly added to the solution was 1.25 g of potassium permanganate with agitation mild enough not to break the fiber. Excess or rapid addition of KMnO_4 was avoided in order to prevent the formation of manganese heptoxide, Mn_2O_7 , which separated as an unstable phase and decomposed on heating into oxygen and manganese dioxide. The beaker was then set in a constant

temperature bath of $35 \pm 1^\circ\text{C}$ for one hour. A small amount of brown gas was evolved as the reaction progressed. The solution mixture also turned brown due to the reduction of permanganated ion to manganese dioxide.

At the end of one hour, the beaker was placed in an ice bath while 20 ml of distilled water was added dropwise. Violent effervescence of purple gas and an increase in temperature were observed. Because of the large heat of mixing of the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system and the formation of Mn_2O_7 from addition of water, a good heat transfer system was essential to avoid explosion. The beaker was then taken and maintained in a boiling water bath for 20 min., while the remaining nitric acid boiled off.

After removing the water bath, 60 ml of water was added to further dilute the solution. The substrate was then taken out of the beaker and treated with 3% hydrogen peroxide to reduce the residual permanganate ion and manganese dioxide to manganese (II) ion. After washing with water and drying in air, the sample was ready for resistivity measurements.

Resistivity Measurements: For the purpose of measuring the resistance of single fibers before and after oxidation, they were mounted on an alumina substrate screen printed with four platinum leads using gold paint for electrical contact. Resistance could then be conveniently measured using the four-point resistance method, which measures the voltage drop across the two center contacts one centimeter apart when a known current is passed through the fiber from the outer two leads. This technique eliminates extraneous effects from lead resistance. For fiber

resistances approaching that of the input resistance of the voltmeter (10 M), a resistance comparison method was employed, yielding a less precise result. In using the four point method, we assume that contact at the surface of a fiber results in an even current distribution in the axial direction in the fiber between the voltage probes, an assumption justified by the large length to diameter ratio of the fiber ($l/d=1000$).

Result and Discussion: Various oxidation procedures have been tested to search for the optimum conditions. Varying the reaction time from 10 min. to 5 hours results in no observable difference in resistivity. This suggests that kinetics in the oxidation step is fast. Different proportions of reactants are also tried and again the differences are not large. Presumably the reactants are so much in excess that their relative amounts do not matter. Also, attempts were made to correlate the degree of oxidation with reaction temperature. It is believed that at temperatures below 20°C the reaction proceeds very slowly, but at temperatures above 45°C complete oxidation would yield mainly CO₂ instead of intercalating the oxygen atoms into the graphite lattice. This series of experiments shows that interstitial oxidation is unfavorable outside this temperature range. However, the relationship between the effectiveness of intercalation and reaction temperature within that range is not well established. The results obtained on Type-P fibers are tabulated in Table I and shown more clearly in Figure 1. Results on different types of fibers are shown in Table II.

From this it can be concluded that the fibers with the best defined graphitic structure produce the largest changes in resistivity. The resistivities of all the samples were found to decrease with time on exposure to atmosphere. A typical decay curve is shown in Figure 2 for an oxidized Type-P fiber. The decay constant in this case is $k = 0.035/\text{day}$ assuming a relationship of

$$\rho = \rho_1 + \rho_0 e^{-kt} \quad (1)$$

where ρ is resistivity.

This relationship suggests a diffusion limited reaction. We suggest that, as prepared, the graphite oxide may have an empirical composition of $C_n OH$ which loses water by the (empirical) reaction

$$2C_{n/2} OH \longrightarrow C_n O + H_2 O \quad (2)$$

and reached an equilibrium distribution of ether and hydroxyl linkages.

Tensile Test: In preliminary studies, single fibers of Type HMS and bundles of GY-70 and Type-P fibers were chemically oxidized as before. Preliminary studies showed that the oxidation process decreased the tensile strength of the fibers, but by no more than 40 percent. Subsequent tests were all performed on single GY-70 fibers and similar results were obtained.

A single fiber of two inches in length was mounted on a thin paper by epoxy glue as shown in Figure 3. The tensile tests were made on an Instron Test Machine. Care was taken to mount the sample on the instrument so that the axis of the fiber and the applied load were properly aligned. The paper was then cut at the middle and testing conducted at a rate of 0.05 cm/min.

Since an oxidized fiber can only be used either for resistivity measurement or a mechanical test, no correlation could be made between the change of resistivity and tensile strength. Yet for each batch treatment where several fibers were oxidized, one fiber was taken for resistivity measurement. A conservative estimate is that the treated fibers all have a resistivity increase in excess of 100 times. Change in mechanical properties is computed based on the average of data obtained on a large number of oxidized and pristine fibers. Table III summarizes the results. It can be concluded that the oxidized fibers do preserve their mechanical strength.

II. Electrochemical Oxidation

Experimental Procedure: A schematic diagram of the apparatus used for the electrolysis is shown in Figure 4. The anode in the circuit was a platinum electrode. The cathode was a single fiber attached to an alumina substrate. Two types of fibers, Type-P and GY-70, were used in these experiments. Leads were connected to the substrate to facilitate resistivity measurements by the four-point method. The electrolyte used was commercially

available concentrated sulphuric acid (95-98%). The electrolysis was carried out in either galvanostatic or potentiostatic conditions. The resistance of the electrolyte was sufficiently high that it could be neglected in the analysis of the electrochemical data.

In galvanolysis, typically a constant current of (2.00 μ amp \pm 1%) was passed through the cell, and the voltage difference between the sample and the reference electrode was recorded continuously. The plateau phenomenon was much less obvious than in the case of oxidizing highly oriented pyrolytic graphite (HOPG) crystals. Usually only three distinct slopes could be observed. This is apparently due to a lower degree of perfection of crystallinity in the fiber. Resistivity measurements were taken periodically.

In the potentiostatic method, the potential between the working and reference electrode was increased stepwise. For each potential the cell current was allowed to reach its steady state value before the increment. The cell was also disconnected for resistivity measurement as the current approached this limiting value. It is possible that different concentrations of ions were intercalated along the fiber axis due to structural imperfections. In order to check against this non-uniform attack, the voltage drop across the sample was recorded separately with currents passed through from both directions when measuring the resistivity. The average of these two absolute values was used.

If it is assumed that there are no reactions at the anode other than oxidation of the fiber, the equivalents of charge intercalated per carbon atom, n can be calculated as

$$n = \frac{t \times i \times 12}{96500 \times W}$$

where t = oxidation time in sec.

i = current in amperes

w = weight of the graphite fiber in grams

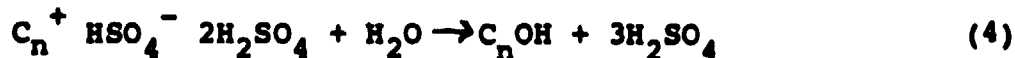
The weight of a single fiber was approximated by assuming the diameter as 10^{-4} m and the density 2 g/cm^3 . The length of the sample was always 1 cm. Using these approximations,

$$n = 79 \times t \times i$$

Electrolytes of different compositions were used to determine the effects of different reactants on the mechanism of graphite oxide formation. Acid concentrations ranged from 1% to 98%. Fuming sulphuric acid was also used to increase the medium's acidity and totally eliminate the presence of water.

Result and Discussion: The results of a constant current and a constant potential electrolysis are shown in Fig. 5 and Fig. 6 respectively. At early stages of the electrolysis the formation of graphite bisulphate is the dominant reaction and the charge intercalated can be approximated closely. In Fig. 6 we see that the resistivity drops steeply during the intercalation of bisulphate ions. The minimum corresponds roughly to a stage 1 compound. At this point, the hydrolysis reaction becomes significant. Further oxidation raises the resistivity back to its

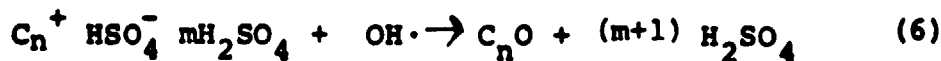
initial value. Partial conversion of graphite oxide to carbon oxides can be expected. The following reactions are believed to take place in the early stages of electrochemical oxidation¹¹:



Graphite oxide is always in equilibrium with graphite bisulphate, and the product during early stages can be expected to be a mixture of two compounds. Once the graphite has been oxidized to a stage-1 bisulphate compound (in equilibrium with some -OH compound) further reaction must proceed by a totally different mechanism. Indeed, Fig. 6 indicates that far more charge is transferred than can be accounted for by further oxidation of the graphite. We suggest that the cathode reaction for this part of the process is



Since the hydroxyl radicals will accumulate in the intercalation compound-solution interface, they could also diffuse into the lattice and we would expect the following reaction.



The sulfuric acid would diffuse out of the lattice as the covalent C-O bonds are formed by the free-radical mechanism. Most of the hydroxyl radicals formed at the cathode would, however, be consumed in reactions with sulfuric acid, probably reducing it to sulfurous acid with water as a byproduct.

The voltage required to form graphite oxide electrochemically (by the method used here) is probably just that voltage required to reduce H_2SO_4 to H_2SO_3 (or H_2O and SO_2), and the graphite reaction might be considered as the side reaction.

Fig. 6 shows that, after recovering its initial resistivity, the resistivity of a fiber increased almost exponentially. Unfortunately, in all of the experiments the fibers broke when the resistivity had increased by about a factor of 10. The breakage always occurred at the contact point. This might be caused by the pressure developed in the interior of the fiber as gaseous carbon oxides are formed through over-reaction, or a structural change that exerts a strain on the fiber, or the dissolution of the gold paste that carries away the fiber. No solution has been found to this breakage problem.

In order to determine the upper limit of the resistivity change, bundles of fibers were oxidized electrochemically. The in situ resistivity measurements were then much less accurate. The problem of non-uniform attack is aggravated, and the small length to diameter ratio yields an uneven current distribution along the fiber axis. Nevertheless, the final resistivity changes were measured with a wheatstone bridge and used for rough comparison. In several cases the change was less than a factor of 3. Either a hindered diffusion into the core of the bundle or an over oxidation to carbon oxides contributes to the small change. In two cases, however, resistivity increased to a factor of 15.

According to the mechanism discussed above, increasing the water content should shift the equilibrium to the right. Hence a less concentrated acid system would be expected to yield better results. The coloring phenomenon seems to indicate some validity of this supposition. In electrochemically oxidizing a bundle of Type-P fiber by dipping it into a 70% H_2SO_4 system, within minutes a blue hue appears in the electrode-gas-liquid interface, while a yellowish green color develops at the tip of the fiber. The hues turn brown upon further oxidation.

A plot of resistivity change vs. potential for single fibers is shown in Fig. 7. Graphite oxide is indeed more easily formed in the more dilute systems. However there is a critical concentration below which the graphite bisulphate compound would just decompose to graphite. Acid concentrations varying from 50% to 90% give similar results.

Fig. 7 also shows that the intercalation of bisulphate ions is most rapid when there is less water present, and the conversion to graphite oxide is more rapid when more water is present. The idea of performing the intercalation of pure H_2SO_4 and the oxidation in a more dilute system seems useful. But once again the breakage problem prevented us from demonstrating the advantage.

In addition, some experiments are performed in fuming sulphuric acid (15-20%). The excess SO_3 would react with the

least traces of water according to the reaction



Spontaneous intercalation is observed. This is understandable in terms of the electrophilic character of SO_3 . Since SO_3 is able to remove electrons from the graphite it acts as an auxiliary oxidizing agent. Resistivity dropped by a factor of 2 by just immersing the sample in the solution. As expected, the increase in the medium's acidity enhances the degree of ionization and minimum resistivity was recorded as $R_0/R=50$. The resistivity does not increase at higher potentials as it does in 96% H_2SO_4 , confirming the mechanism that the presence of H_2O is essential in forming graphite oxide.

It is also speculated that the intercalation will be best accomplished electrochemically and the oxidation chemically. The fiber is electrochemically synthesized to the stage 1 graphite bisulphate compound and then placed in the oxidizing mixture (Hummer's method) with H_2O in it. Since the charge intercalated can be carefully controlled, it seems possible to have a consistent starting composition for the oxidation and hence a reproducible result. Unfortunately all the fibers treated this way break in the chemical oxidation step. Whether that is due to some unknown reactions is uncertain.

Comparing the electrochemical method to the chemical one indicates that the former does not yield as good a result in terms of increase in resistivity. This can be explained by the difficulty in exchanging the hydroxyl ions with the bisulphate ions. Graphite bisulphate tends to form a highly stable residue compound by trapping the intercalates at defect sites. Hennig¹² suggest that about 1/3 of the intercalated bisulphate ions and about 1/2 of the H₂SO₄ molecules remain in the lattice during de-intercalation. Another factor attributable to the difference in results might be an alternative mechanism taken by the chemical method. Ubbelohde¹³ suggests that OH radicals might form in the presence of position ions as described by the equilibrium



If indeed the equilibrium was sufficiently shifted to the right, the formation of graphite oxide might not have to go through the sequence where oxidation is preceded by the intercalation of bisulphate ions. These energetic radicals may directly bond to the graphite lattice. Also noteworthy is that the constant current method cannot accomplish the same goal as in the constant potential electrolysis. It is only at high potentials that hydroxyl ions can be generated and enough energy is provided to overcome the positive ΔG of reaction.

CONCLUSION

The electrical resistivity of commercial carbon graphite fibers has been successfully increased by using chemical oxidation techniques. The resistivity of the oxidized fiber was observed to decline exponentially with time on exposure to atmosphere. Still the final stabilized value is three orders of magnitude greater than the pristine fiber. Best results are obtained on the highly graphitized fibers.

Although the electrochemical techniques do not render a resistivity increase as dramatic as in the chemical treatment, it provides a controllable method of synthesis. An increase in excess of 10 times can be obtained and no decomposition is detected.

Tests on tensile strength and elastic modulus indicate that fibers do maintain their mechanical properties after treatment. The interstitial oxidation reduces the strength of the fiber by no more than 25%.

The results of this investigation have been positive with respect to the original proposal of increasing the resistivity of the fiber and at the same time maintaining the high mechanical strength. The feasibility of controlled electrolytic oxidation is also confirmed. It is possible that a resistivity increase of an order of magnitude would be enough to prevent the airborne fibers from causing arc over problems. The electrochemical oxidation of the fibers would then provide an ideal solution to the problem stated.

REFERENCES

1. NASA TM 78652-January 1978
2. U.S. Department of Commerce News ITA 78-73--January 20 1978
3. Time Magazine, March 13, 1978 p.90
4. Hofmann, U., Holst, R. 1939, Berichten 72:754
5. Hennig, G.R. 1959. Progr. Inorg. Chem. 1:125-205
6. Croft, R.C. 1960 Q. Rev. 14:1-49
7. Carr, K.E. 1970 Carbon 8:245-47
8. Scholtz, W., Boehm, H.P. 1969 Z.Anorg. Allg. Chem. 369:327-40
9. Van Doorn, A.B.C., Groenewege, M.P., de Boer, J.J. 1963
K. Ned Akad. Wet. Ser. B66:165-72
10. Hummers, W.S., Offeman, R.E., 1958 J. Am. Chem. Soc. 80:1339
11. Bottomley, M.J., Parry, G.S., Ubbelohde, A.R., Young, D.A. 1963
J. Chem. Soc. pp 5674-80
12. Hennig, G. 1951 J. Chem. Phys. 19:922-29
13. Ubbelohde, A.R. 1935 J. Chem. Soc. p 1605

Table I. Correlation of resistivity change with reaction temperature for Type P fiber.

| Temperature °C | Ratio of increase in Resistivity | Number of samples | Standard Deviation |
|-------------------|-------------------------------------|----------------------|-----------------------|
| 25 | 1250 | 4 | 622 |
| 30 | 1440 | 3 | 260 |
| 35 | 1080 | 6 | 513 |
| 40 | 2190 | 4 | 830 |
| 45 | 1880 | 6 | 465 |
| 50 | 1390 | 3 | 526 |
| 60 | 620 | 1 | 0 |

Table II. Summary of resistivity changes in graphite fibers.

| Fiber type | Resistivity Increase (R/R_0) | |
|------------|----------------------------------|------------------|
| | Initial Value | Stabilized Value |
| Type P | 10^4 | 2×10^3 |
| GY-70 | 2×10^3 | 5×10^2 |
| HMS | 10 | 10 |
| CTT-30 | 2 | 2 |
| HT | 2 | 2 |

Table IIIa. Mechanical Strength of Pristine GY-70 Fibers

| No. of Samples | Avg. Tensile Strength (10^9 Pa) | Avg. Elastic Modulus (10^{11} Pa) |
|----------------|------------------------------------|--------------------------------------|
| 100 | 1.45 ± 0.13 | 4.18 ± 0.41 |

Table IIIb. Mechanical Strength of Oxidized GY-70 Fibers

| Sample No. | Break Load (g) | Tensile Strength (10^9 Pa) | Elastic Modulus (10^{11} Pa) | Percent Change | |
|------------|-----------------|-------------------------------|---------------------------------|------------------|-----------------|
| | | | | Tensile Strength | Elastic Modulus |
| 1 | 10.4 | 1.35 | 3.75 | | |
| 2 | 6.08 | .79 | 2.63 | | |
| 3 | 6.80 | .88 | 2.44 | | |
| 4 | 8.36 | 1.08 | 4.56 | | |
| 5 | 10.6 | 1.38 | 3.84 | | |
| 6 | 11.6 | 1.50 | 3.45 | | |
| 7 | 9.92 | 1.29 | 3.07 | | |
| 8 | 11.3 | 1.47 | 3.50 | | |
| Average | 9.38 ± 0.20 | 1.22 ± 0.25 | 3.40 ± 0.71 | 15.9% | 18.7% |

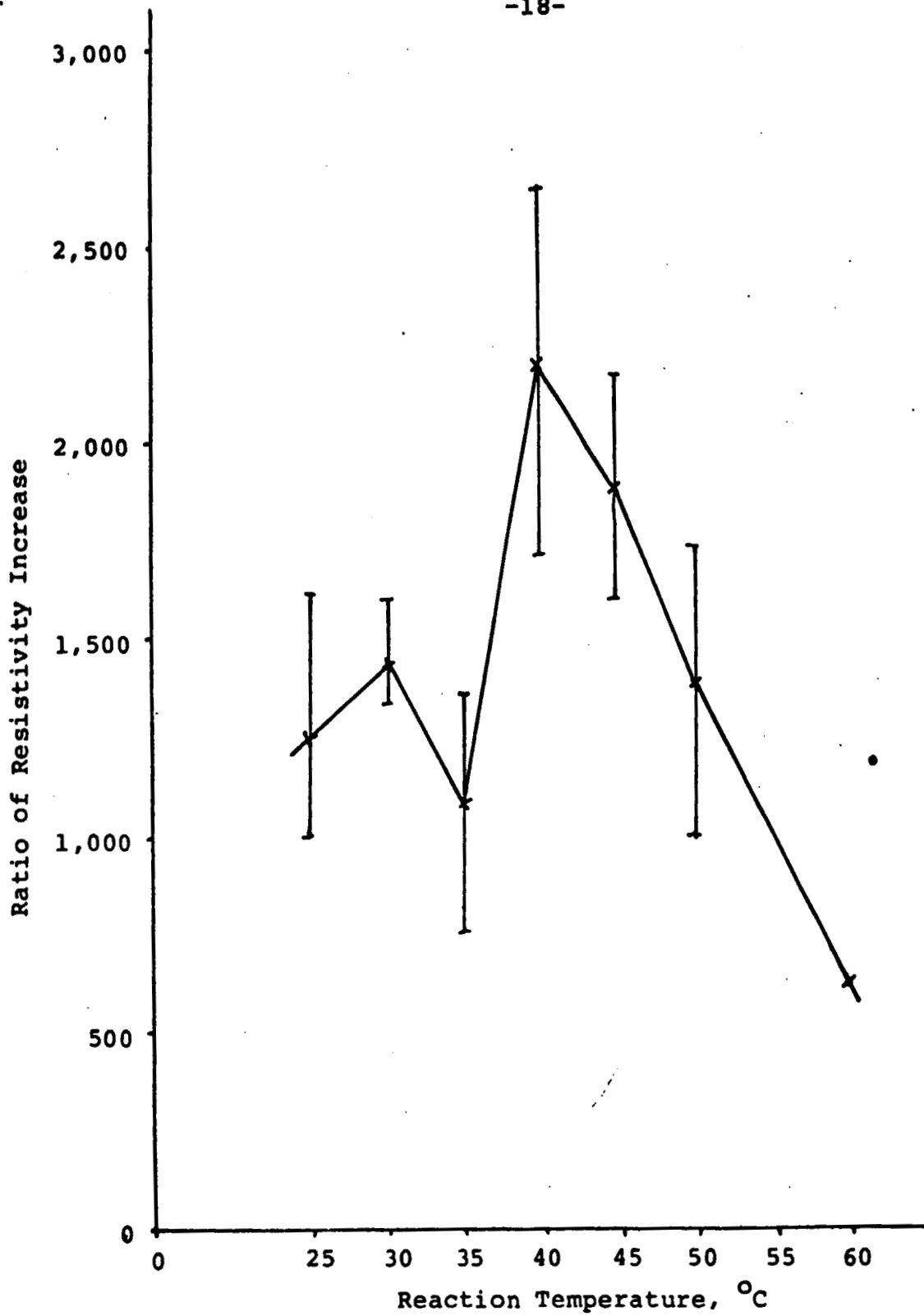
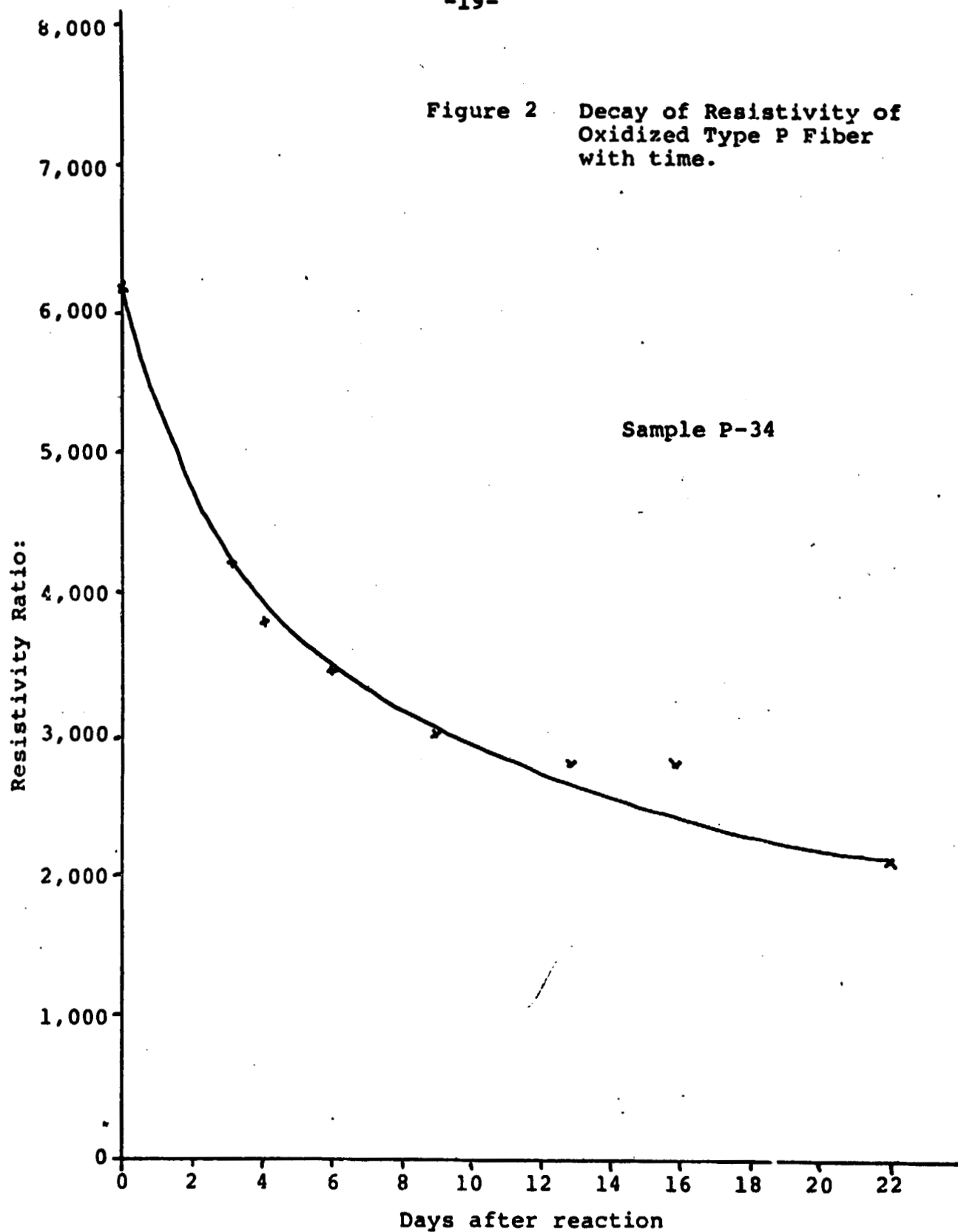


Fig. 1 Resistivity change of the oxidized Type-P fiber as a function of reaction temperature.

Figure 2 Decay of Resistivity of Oxidized Type P Fiber with time.



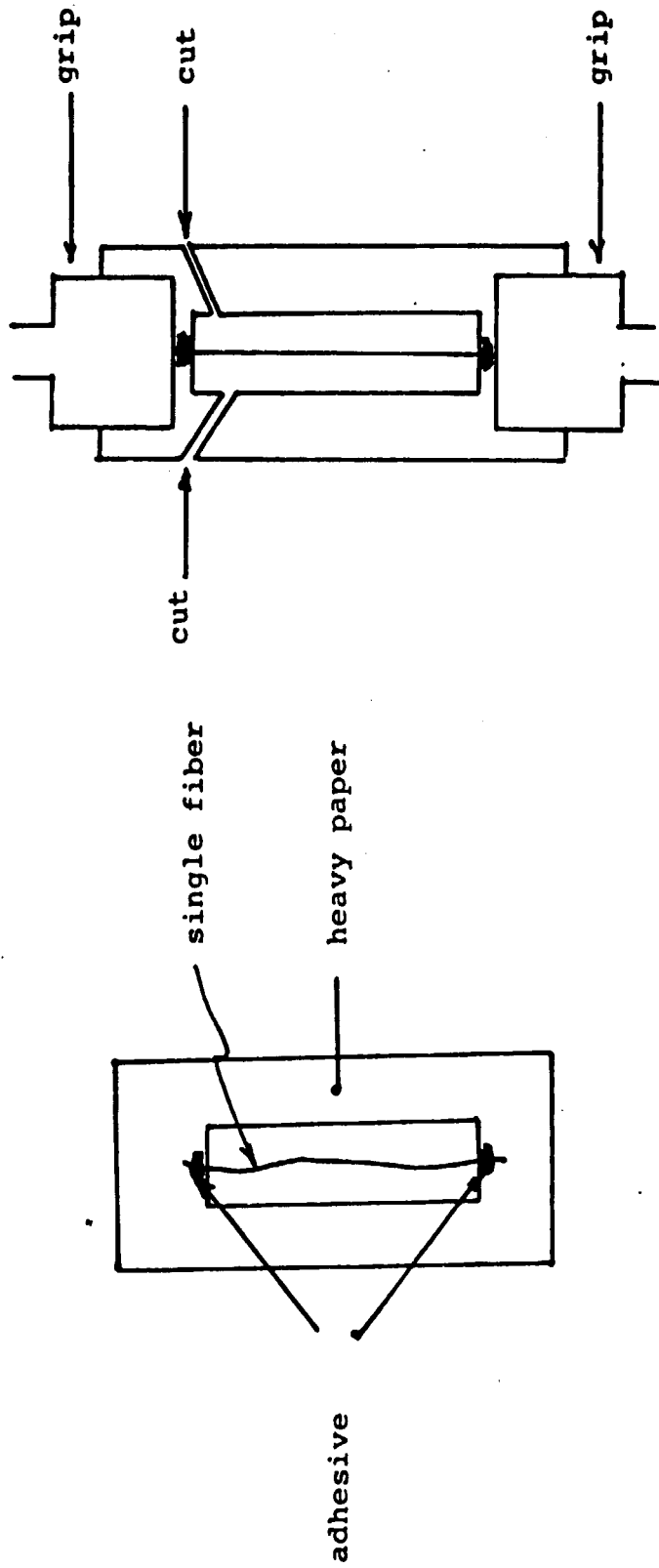


Figure 3 Single Fiber Tensile Test Method.

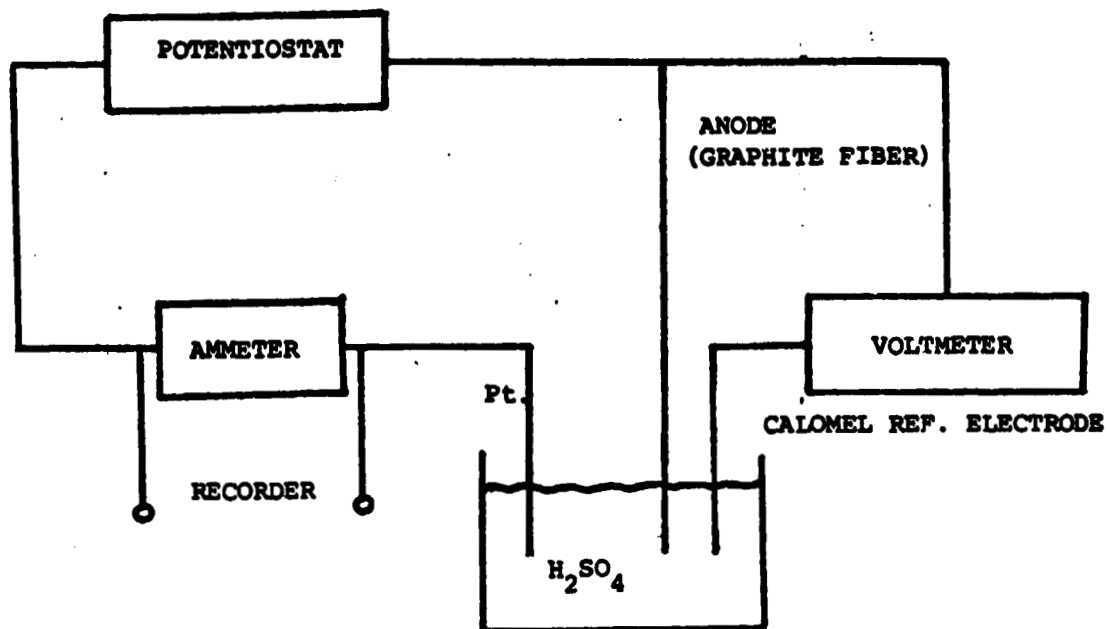


Fig. 4 Experimental set-up of the Electrolysis

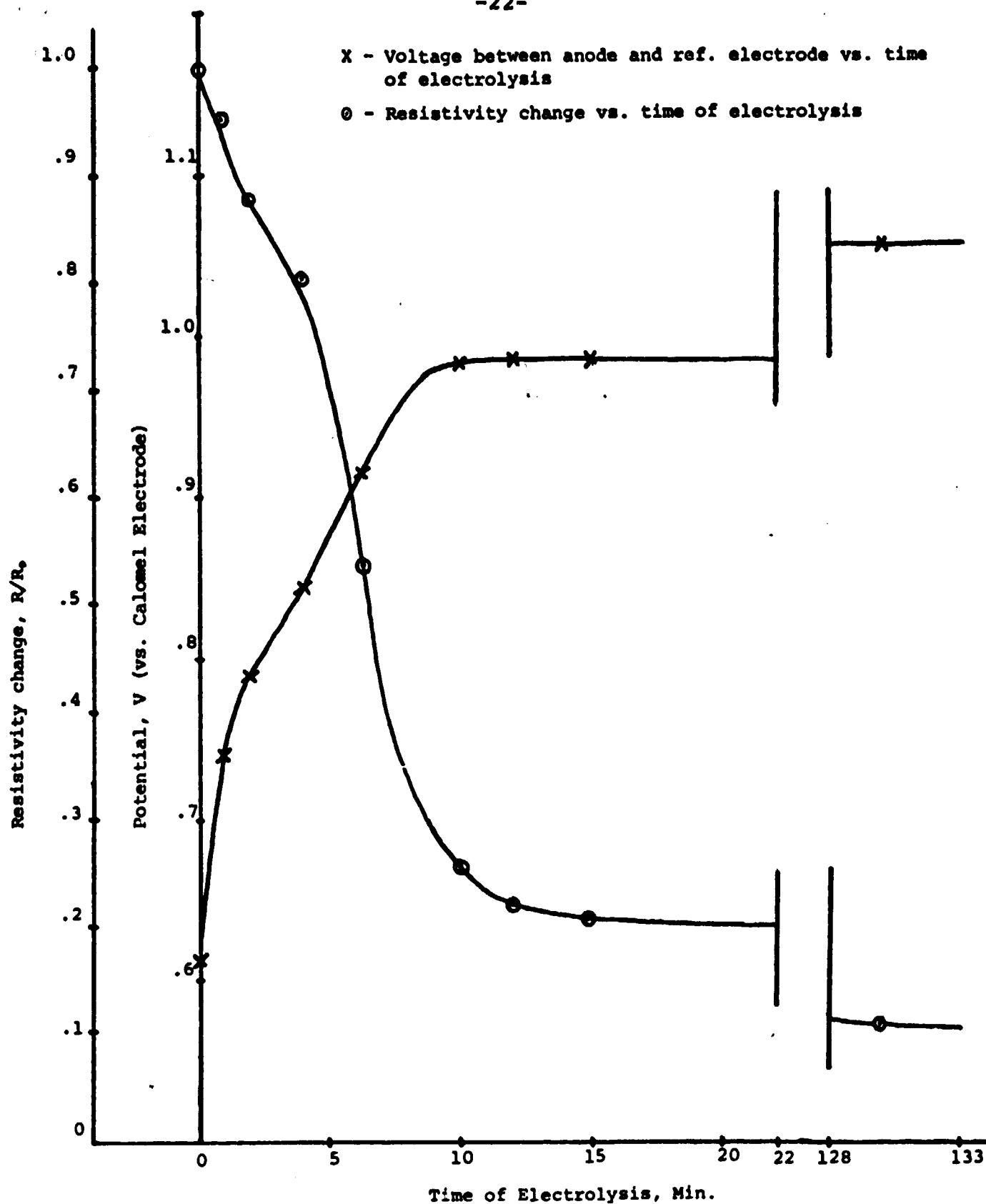


Fig. 5 Constant Current Electrolysis of a Single GY-70 Fiber at $2.00 \pm 1 \mu A$

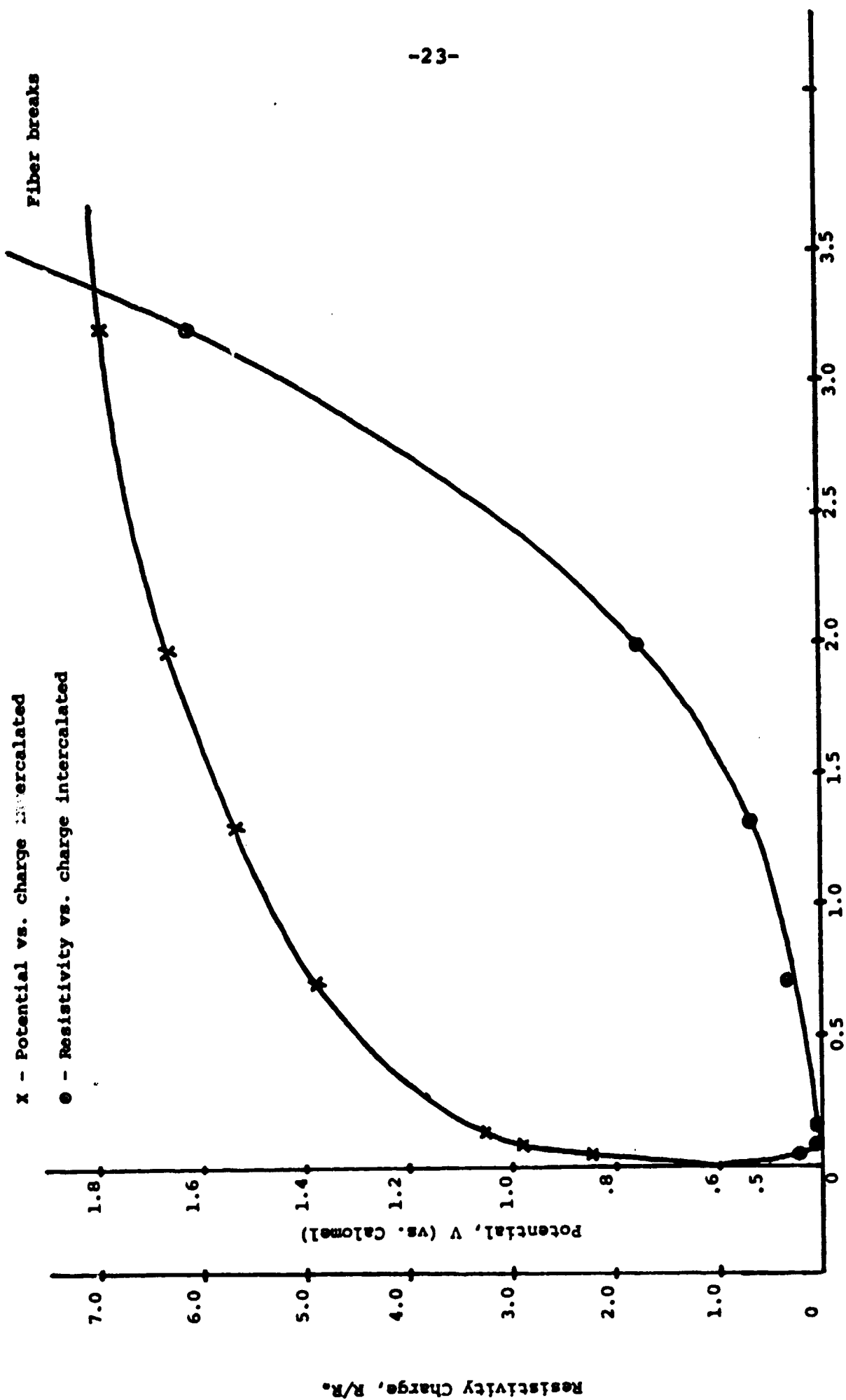


Fig. 6 Potentiostatic Electrolysis of a single GY-70 Fiber

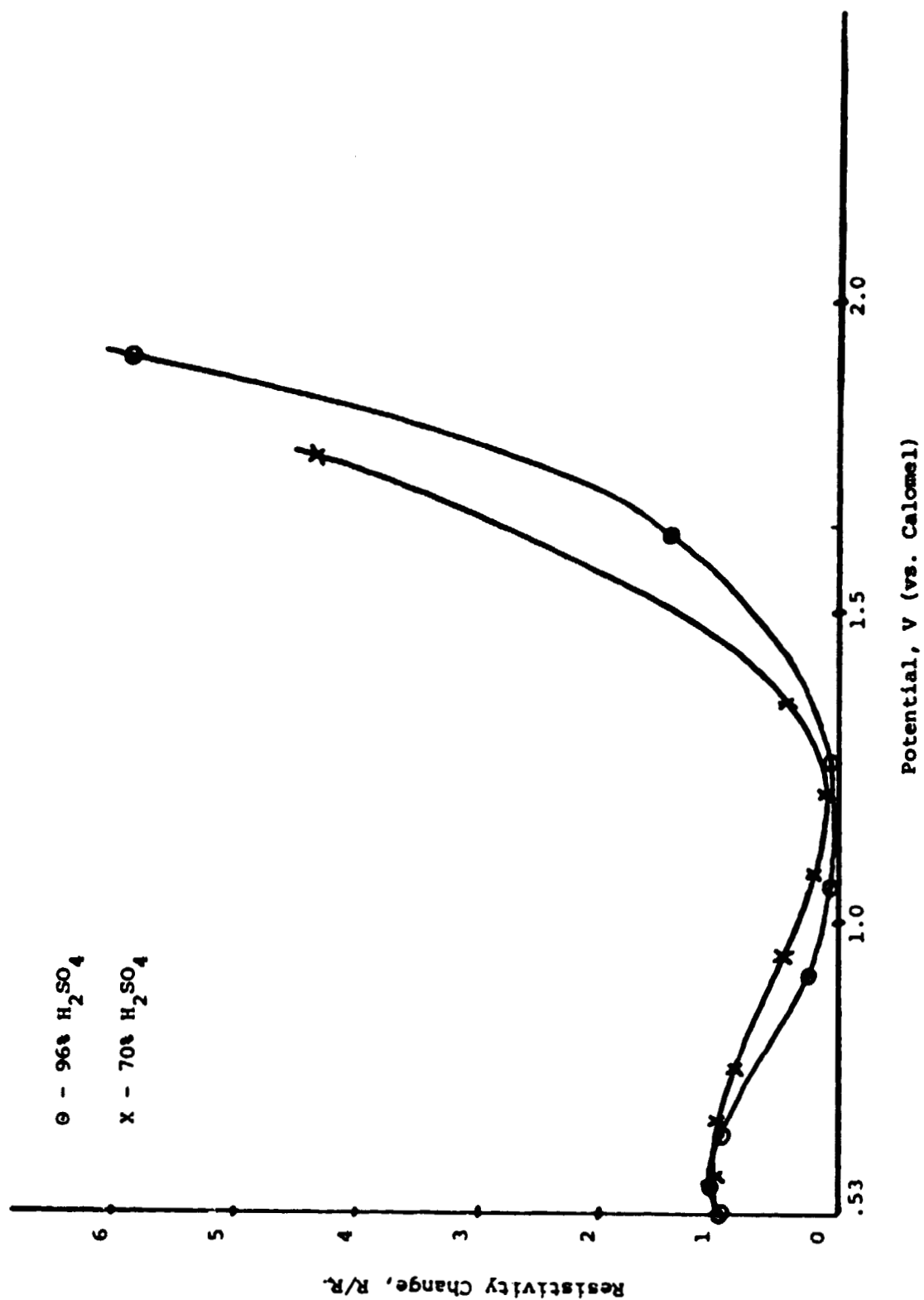


Fig. 7 Electrolysis of a Single GY-70 Fiber in 70% H_2SO_4 and 96% H_2SO_4